Chemical Engineering Journal 162 (2010) 242–249

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Ammonia removal from aqueous solutions using hollow-fiber membrane contactors

S.N. Ashrafizadeh*, Z. Khorasani

Research Lab for Advanced Separation Processes, Department of Chemical Engineering, Iran University of Science & Technology, Narmak, Tehran 16846, Iran

ARTICLE INFO

Article history:
Received 3 December 2009
Received in revised form 15 May 2010
Accepted 18 May 2010

Keywords:
Hollow fiber
Membrane
Ammonia
Wastewater
Polypropylene

ABSTRACT

The adverse effects of ammonia and related compounds commonly found in wastewater streams have promoted the development of more efficient methods for their removal. In this study, polypropylene hollow-fiber membranes were used to achieve this purpose. A dilute solution of sulfuric acid was used as a stripping solution to accelerate the removal of the ammonia from aqueous solutions. The effects of several factors such as the initial concentrations of the ammonia and sulfuric acid solutions, the pH of the ammonia feed, the velocity of the feed streams and the presence of excess ions in the ammonia feed solution on the overall mass transfer of the ammonia were investigated. The Taguchi method was used to design the experiments and analyze the results.

Polypropylene hollow-fiber membranes were found to be very effective in separating ammonia from the waste waters, in proper conditions, ammonia removal of over 99% was achieved. Results show that the initial concentrations and velocities of the ammonia and sulfuric acid solutions had negligible effects on the ammonia removal in the range studied. Increasing the pH value of ammonia feed solution up to 10 improved the removal of ammonia significantly while further increasing the pH to the higher values resulted in insignificant improvements. Raising the ammonia feed velocity enhanced the ammonia removal in the range studied.

1. Introduction

Ammonia is a common contaminant in both municipal and industrial wastewaters. The concentration of NH_3–N may vary from 5 to 1000 mg/L in industrial wastewater such as coking, chemical fertilizer, coal gasification, petroleum refining, pharmaceutical and catalyst factory [1]. The ammonia concentration in the municipal waste may vary from 10 to 200 mg/L [2]. The presence of excessive amounts of nitrogen compounds in the receiving streams can cause a significant pollution burden. The potential drawbacks of the nitrogen release in the water streams involve decreased dissolved oxygen required for the aquatic life, toxic effects on fish, reduced disinfection efficiency and accelerated corrosion of metals and construction materials. The removal of nitrogen compounds is thus required to protect both the environment and human health [1,2].

Treatment methods for ammonia removal include nitrification–denitrification, break point chlorination, chlorination–dechlorination, air/steam stripping, ion exchange and adsorption [1–5]. However, all these methods have limitations and shortcomings. Conventional methods for ammonium and organic removal from the municipal and industrial wastewaters are mostly based on biological treatments [4]. However, the effectiveness of these processes is restricted by slow bioconversion and unfavorable environmental factors. On the other hand, it is difficult to treat wastewater by a conventional biochemical process when its NH_3–N concentration is higher than 300 mg/L. In these cases the ammonia concentration must be reduced prior to biochemical treatment [5,6]. Chlorination and ion-exchange processes have also occasionally been applied to industrial wastewaters containing high levels of ammonia. However, the disadvantages are their high cost and difficult maintenance due to the chemicals used in the oxidation and regeneration steps [4,7,8].

Development of hollow-fiber membrane contactors provides an attractive alternative for the removal of volatile contaminants such as ammonia [9]. A membrane contactor is a device that achieves liquid/liquid and gas/liquid mass transfer without the dispersion of one phase within another. The hollow fibers used are commonly microporous and hydrophobic. In the case of the gas/liquid separation, the membrane prevents aqueous solution, which has higher surface tension penetrating gas-filled pores, since it is hydrophobic. The volatile compound will volatilize from the feed, diffuse through the gas-filled membrane pores, and can then be swept away by a sweep gas, sucked up by a vacuum or reacted with a stripping solution [10,11]. Compared to conventional absorption or stripping processes, such as bubble columns and packed beds, the use of hydrophobic hollow-fiber membrane contactors provides a

---

* Corresponding author. Tel.: +98 21 77240496; fax: +98 21 77240495.
E-mail address: ashrafi@iust.ac.ir (S.N. Ashrafizadeh).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.05.036

number of advantages. These include: a larger interfacial area per unit volume, which provides fast removal of the volatile contaminants; independent control of gas and liquid flow rates without causing any flooding, loading or foaming; the lack of production of any secondary pollutants and the possibility of recovery and reuse of volatile compounds. Furthermore, due to the tangential nature of the flow in the membrane contactors, the gas stripping process does not require operation at a high-pressure drop. This also contributes to lower capital cost and ease of operation [11–15].

In this process, the feed and stripping solutions were flowing on either side of a membrane and the hollow-fiber membrane provided a barrier between two liquid phases. It was the aim of this work to investigate the performance of polypropylene hollow-fiber membrane contactors for ammonia removal from aqueous solutions under different processing conditions and to define the operational parameters necessary to remove ammonia efficiently. The factors investigated are the initial concentrations of the ammonia and sulfuric acid solutions, the pH of the ammonia feed solution, the feed stream velocities and the presence of excess electrolytes in the feed solution. Other researchers using membrane contactors as a technique of ammonia removal have investigated the effect of different parameters individually [14,15]. In this work, we investigate the possible effect of parameters upon each other using the Taguchi method for experimental design.

A common approach to optimize operating parameters of a particular process is to perform all or some of the possible experiments employing one at a time, i.e. varying a parameter while keeping the others constant, or trial and error methods with the design variables to find a feasible or optimum condition. Such an approach may be time consuming and expensive when multiple factors are involved. To prevent this problem, experimental design can be achieved using factorial design. This technique aims to discover the combinations of factors that give the best combination. However, employing a full factorial experimental design is restricted when many factors and levels are studied [16,17]. Analysis of variance (ANOVA) was used to analyze the results of the experiments and to determine the contribution of each influencing factor [18,19]. Thus, the Taguchi method was employed for experimental design while the ANOVA technique was used for data analysis.

2. Materials and methods

2.1. Reagents

All chemicals used were analytical grade reagents from Merck. All aqueous solutions and dilutions were prepared using distilled water. Solutions containing ammonia were prepared through addition of measured volumes of ammonium hydroxide to distilled water. Aqueous ammonium solutions were buffered with potassium dihydrogen phosphate and di-potassium hydrogen phosphate. The stripping solution was prepared through the addition of specified volumes of sulfuric acid to distilled water. Sodium chloride salt was used to investigate the effect of presence of excessive ions on the ammonia removal. The ammonia concentration in the solution was analyzed by Nesslerization [20]. The concentration of ammonia in the samples was measured using a UV–visible Scanning Spectrophotometer, Camspec M350 model [20].

2.2. Membrane contactor

A laboratory-scale membrane contactor with polypropylene microporous hollow fibers from Liqui-Cel Company was used. More details on the specifications of this module are given in Table 1.

Table 1
Specifications of the hollow fiber membrane contactor.

Hollow-fiber membrane module	2.5 × 8 Liqui-Cel membrane
Membrane fiber/potting material	Polypropylene/polyethylene
Fiber OD/ID	300/220 μm
Membrane porosity	40%
Liquid flow limits	
Shell side	0.16–1.8 m^3/h
Lumen side	0.1–0.7 m^3/h
Priming volume	
Shell side	0.4 L
Lumen side	0.15 L
Maximum shell side allowable working temperature/pressure	40 °C, 7.2 bar 70 °C, 2.0 bar
Maximum lumen side allowable working temperature/pressure	15–25 °C, 4.8 bar
Pore diameter	0.03 μm
Shell side geometric void fraction	0.40

2.3. Experimental procedure

The setup for ammonia removal is shown in Fig. 1. The ammonia feed solution was pumped through the lumen of the hollow-fiber membrane, while the stripping solution containing sulfuric acid was pumped into the shell side of the hollow-fiber membrane. Both solutions were recycled to their respective reservoirs. All the experiments were carried out at about 20 °C and a thermometer was installed in each reservoir to measure the temperature of the solutions during the experiments. According to Eq. (1) the reaction between NH_4OH and H_2SO_4 is exothermic and thus the ammonia feed temperature was slightly increased during the experiments. Therefore a cooling water system was used to maintain the temperature constant. The hydrophobic membrane isolated the two aqueous solutions and the ammonia diffused across the micropores in the membrane wall, but water could not pass through the hydrophobic membrane. As a result, the ammonia in the raw solution decreased by reaction forming ammonium salt in the acid solution.

$$2NH_4OH + H_2SO_4 \rightarrow (NH_4)_2 + SO_4 + 2H_2O + Q \qquad (1)$$

2.4. Analytical procedure

At regular time intervals, 1 mL samples were taken from the feed solution and were immediately diluted to a certain volume. The concentration of ammonia was then determined by Nesslerization tests of the dilute solutions. Each experimental result reported is the arithmetic mean of at least two replicate experiments.

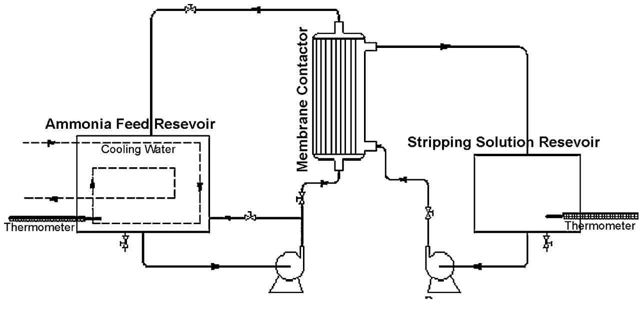

Fig. 1. The schematic representation of the experimental set up.

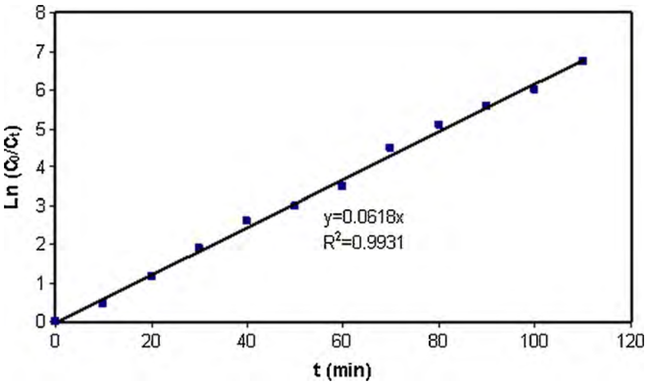

Fig. 2. Typical results showing the procedure of *K* determination.

2.5. Determination of overall mass transfer coefficient

The overall mass transfer coefficient, *K*, was determined experimentally as follows [14]:

$$K = \frac{V}{At} \ln \frac{C_0}{C_t}, \tag{2}$$

where, K, V, A, C_0 and C_t are the overall mass transfer coefficient, total volume of feed solution, membrane surface area, concentration of ammonia at initial and time t in the bulk feed solution, respectively. Therefore, plotting $\ln(C_0/C_t)$ vs. t yielded a straight line. Typical results are shown in Fig. 2. Using Eq. (2) the overall mass transfer coefficient, *K*, can be calculated from the slope of the line.

2.6. Experimental design

2.6.1. Theoretical background of the Taguchi method

The Taguchi method was used to design the experiments. Different steps of the Taguchi approach to experimental design are [16–17,21]:

I. Determine the quality characteristic to be optimized. Quality characteristic is the output or the response variable to be observed.

II. Identify the noise factors and test conditions. Noise factors are those parameters which are either uncontrollable or are too expensive to control.

III. Identify the control parameters and their alternative levels. Control parameters are those design factors that can be set and maintained. The number of levels for each test parameter defines the experimental region.

IV. Design the matrix experiment. The Taguchi has many standard orthogonal arrays and corresponding linear graphs for the control parameters to fit a specific study. For this study, an L orthogonal array was selected based on the number of factors and levels. These are shown in Tables 2 and 3.

V. Conduct the matrix experiment. A matrix experiment consists of a set of experiments in which the settings of the various parameters are varied.

VI. Analyze the data and determine the optimum parameter configuration after the experiments are conducted. To analyze the results, the Taguchi method uses a statistical measure of performance called the signal-to-noise (SN) ratio. The SN ratio, the ratio of the mean (signal) to the standard deviation (noise), is a performance measure to choose control levels that best cope with noise. The SN equation depends on the criterion for the quality characteristic to be optimized. While there are many different possible SN ratios, three of them are considered standard and are generally applicable in the most situations: biggest-is-best, smallest-is-best and nominal-is-best. Whatever the type of quality or cost characteristic, the transformations are such that the SN ratio is always interpreted in the same way. For the larger the better, as in this study, the following relation is used for SN calculation:

$$\mathrm{SN} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{K^2}\right), \tag{3}$$

where n is the number of experiments and K is the response of each experiment that is the overall mass transfer of ammonia and was calculated according to Eq. (2). Notice that the SN ratio is expressed on a decibel scale.

VII. Predict the performance at these levels. When the Taguchi method is used for experimental design, the predicted optimum setting need not correspond to one of the rows of the matrix experiment. This is often the case when highly fractioned designs are used. Therefore, as the final step, an experimental confirmation is run using the predicted optimum levels for the control parameters being studied.

2.6.2. Experimental procedure

The experiments were performed in two stages. In the first stage, the effect of five variables on the overall mass transfer of the ammonia was investigated. The variables investigated were: the initial concentration of ammonia, the pH of the ammonia feed, the veloci-

Table 2
Value of mass transfer coefficient obtained in various runs.

Run	Parameters					
	Ammonia feed velocity (m/s)	Ammonia feed pH	Ammonia feed initial concentration (ppm)	V_{Acid} (m/s)	Salt concentration (M)	$K \times 10^5$ (m/s)
1	0.053	8	50	0.025	0	0.1206
2	0.053	9	200	0.05	0.5	0.6354
3	0.053	10	400	0.1	1	1.0923
4	0.053	11	800	0.2	1.5	1.1786
5	0.106	8	200	0.1	1.5	0.1219
6	0.106	9	50	0.2	1	0.6673
7	0.106	10	800	0.025	0.5	1.2075
8	0.106	11	400	0.05	0	1.3113
9	0.160	8	400	0.2	0.5	0.1225
10	0.160	9	800	0.1	0	0.6871
11	0.160	10	50	0.05	1.5	1.2739
12	0.160	11	200	0.025	1	1.3928
13	0.213	8	800	0.05	1	0.1230
14	0.213	9	400	0.025	1.5	0.6998
15	0.213	10	200	0.2	0	1.3188
16	0.213	11	50	0.1	0.5	1.4570

Table 3
Amount of mass transfer coefficient in various runs.

Run	Parameters			
	Ammonia feed velocity (m/s)	Ammonia feed pH	Stripping solution initial concentration (%)	$K \times 10^5$
1	0.106	11	3	1.3135
2	0.106	12	5	1.3255
3	0.106	13	7	1.3270
4	0.160	11	5	1.3928
5	0.160	12	7	1.4065
6	0.160	13	3	1.4070
7	0.213	11	7	1.4473
8	0.213	12	3	1.4607
9	0.213	13	5	1.4623

ties of the ammonia feed and stripping solutions, and the presence of excess ions in the ammonia feed solution. The temperature of both solutions was kept at 20 °C and the stripping solution consisted of 5% sulfuric acid. To perform the experiments, levels were chosen for each factor based upon theoretical facts and experimental limitations. Table 2 demonstrates the results of Taguchi design for the first experimental stage. The second stage of experiments was performed using the results obtained from the first stage. This time the effect of three variables including the pH of the ammonia feed, the ammonia feed velocity and the concentration of the stripping solution on the overall mass transfer of ammonia was studied. The temperature of both solutions was kept at 20 °C and the ammonia feed concentration was set at 800 ppm. The stripping solution velocity was fixed at 0.025 m/s. Table 3 shows the experimental results for the second stage of experiments.

3. Results and discussions

3.1. First stage of experiments

3.1.1. Profile of ammonia concentration vs. time

Fig. 3 illustrates how ammonia concentration varied with time. It was observed that in all of the performed runs, except runs 1, 5, 9 and 13, ammonia was almost completely removed from the aqueous solution. Further analysis showed that this was due to the low pH (pH 8) of the feed solution in these runs which prevented the conversion of NH_4^+ into NH_3 [2].

3.1.2. Effect of different variables upon ammonia removal

In order to investigate the effect of different parameters on the membrane performance, the overall mass transfer coefficient, K, was determined in each run, using the procedure described in Section 2.5. Table 2 displays the results obtained. Using the mean response, i.e. arithmetic mean of the obtained K values as mentioned in Section 2.4, [16–18] we then investigated how each parameter influenced the overall mass transfer coefficient. The effect of each parameter on the K value is illustrated in Fig. 4. Qualitek-4 is statistic-based commercially available software to design and analyze Taguchi experimental design method. Meanwhile, the ANOVA, analysis tool of this software, was used to determine the contribution of each parameter to the variation of overall mass transfer coefficient (Table 4).

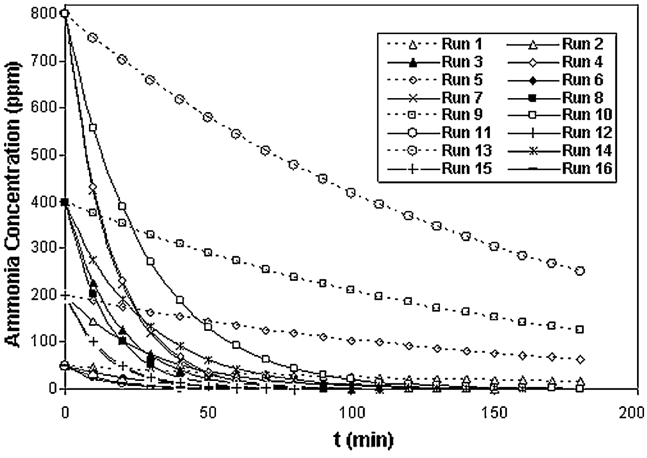

Fig. 3. Ammonia concentration vs. time.

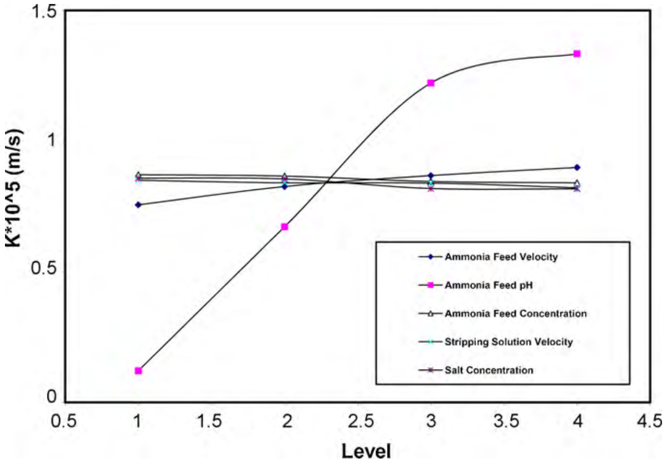

Fig. 4. Effect of different parameters on overall mass transfer coefficient.

As demonstrated in Fig. 4 the overall mass transfer coefficient increased noticeably with increasing pH over the range 8–10. However, as the pH further increased to 11, the mass transfer coefficient was promoted with a lower degree. This might be due to the considerably low concentration of NH_4^+ at the pH values higher than 11 [2].

It is also observed that increasing the ammonia feed velocity increased the overall mass transfer coefficient. The improvement in the overall mass transfer coefficient might be due to the fact that there is a transfer boundary layer near the wall of the membrane which becomes thinner as the ammonia feed flow rate increases. Consequently, the stripping rate of ammonia was enhanced as the feed velocity was increased (due to a decrease in the liquid film

Table 4
Contribution of each parameter on overall mass transfer coefficient.

Parameter	Contribution (%)
pH of the ammonia feed solution	96
Velocity of the ammonia feed solution	2.8
Concentration of ammonia in the feed solution	0.5
Velocity of the acid solution	0.5
Salt concentration	0.3

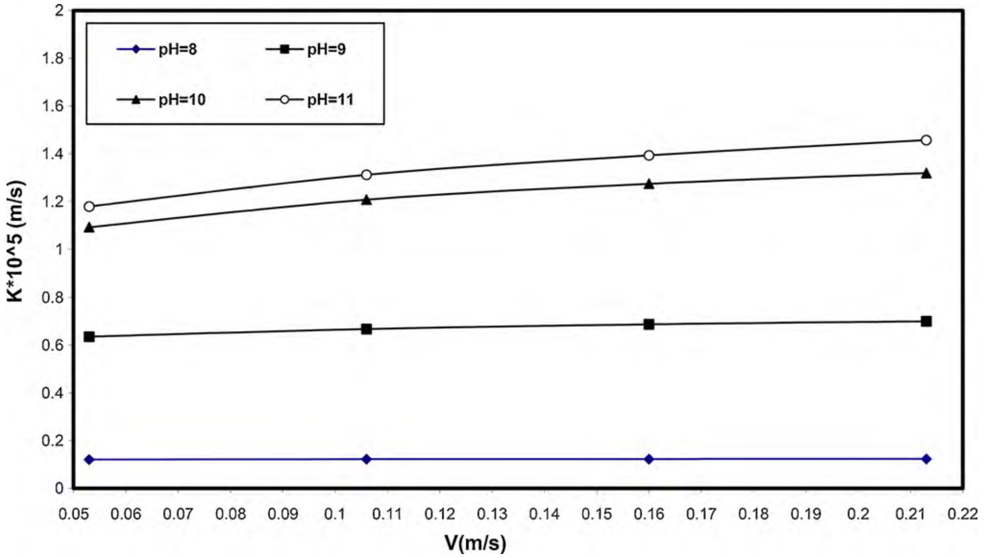

Fig. 5. Effect of ammonia feed velocity on overall mass transfer coefficient at different ammonia feed pH values (other parameters are at their optimum values).

resistance). As it was observed, the velocity of the acid solution did not have the same effect and imposed a negligible effect on the ammonia removal. This further confirms that the reaction between ammonia and acid takes place at the interface of the acid solution which is in contact with the membrane's outer surface.

The initial concentration of the ammonia and the amount of excess ions did not affect the overall mass transfer coefficient. As long as the amount of sulfuric acid in the system was sufficient to remove the ammonia, the stripping process continued ensuring the independency of ammonia removal from the ammonia initial concentration. In other words, the feasibility of using hollow-fiber membrane contactors for the treatment of wastewaters in a very broad range of ammonia concentrations was confirmed. Meanwhile, since diffusion of ammonia through the membrane pores was independent of the existing electrolytes in the aqueous solution; it is reasonable that this variable does not influence the ammonia removal. This independency is an advantageous characteristic of hollow-fiber membrane contactors compared to other methods which are restricted to either a particular range of ammonia concentration or are sensitive to the presence of excess ions in the ammonia solution.

According to the results exhibited in Table 4, the pH of the ammonia feed played the most important role in the ammonia removal; after that the ammonia feed velocity was the most effective parameter. All other parameters imposed negligible effects on the overall mass transfer coefficient and hence on the ammonia removal. The results are sensible according to the above explanations.

The optimum conditions, according to the software analysis, were ammonia feed pH and velocity at their maximum and the other parameters at their minimum values. However, the values of the stripping solution velocity and the salt concentration had negligible effects on the ammonia removal where lowering the initial ammonia concentration resulted in a faster removal of ammonia.

3.1.3. *Effect of pH and velocity of the feed solution*

Since ammonia feed velocity and pH proved to be the most effective parameters in ammonia removal, their effects on the overall mass transfer coefficient were studied while the other parameters were kept at their optimum conditions. These results are illustrated in Fig. 5. This Figure shows that increasing the pH improved the overall mass transfer significantly up to pH 10 while a further increase to 11 resulted in only a slight improvement.

On the other hand, at lower values of the pH, an increase in the ammonia feed velocity led less effective on the overall mass transfer coefficient than when the pH was at the upper end of its range (i.e. 8). This phenomenon may be due to the fact that at low pH values the majority of ammonia was not converted to free ammonia [2] and thus substantial mass transfer did not take place. Increasing the feed velocity did not significantly affect the ammonia removal because there was not enough free ammonia to be removed.

3.1.4. *Effect of initial concentration of the ammonia in the feed*

Fig. 6 displays the scaled ammonia concentration vs. time for different initial concentrations of ammonia in the feed solution. All other parameters are at their optimum conditions. It can be seen that the initial concentration of ammonia had a negligible effect on ammonia removal. The overall mass transfer coefficient was about 1.47×10^{-5} (m/s) for all of the runs conducted. Since other techniques of ammonia removal are only effective for a specific range of ammonia concentration, this characteristic of membrane contactors makes them superior to many other methods of ammonia removal.

3.1.5. *Effect of stripping solution velocity*

Fig. 7 shows the scaled ammonia concentration vs. time for various stripping solution velocities (all other parameters were at

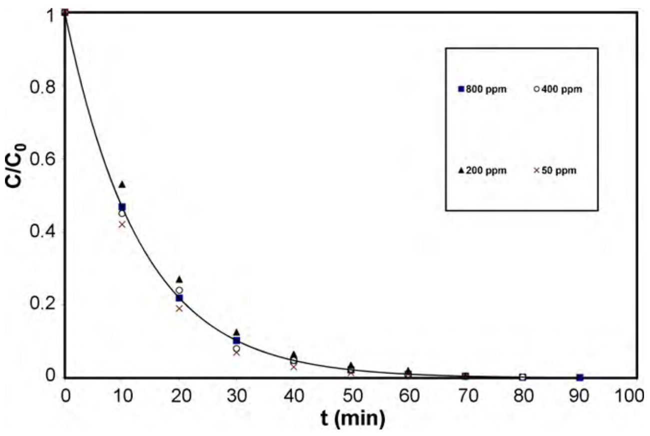

Fig. 6. Ammonia concentration vs. time at different ammonia feed initial concentrations (other parameters are at their optimum values).

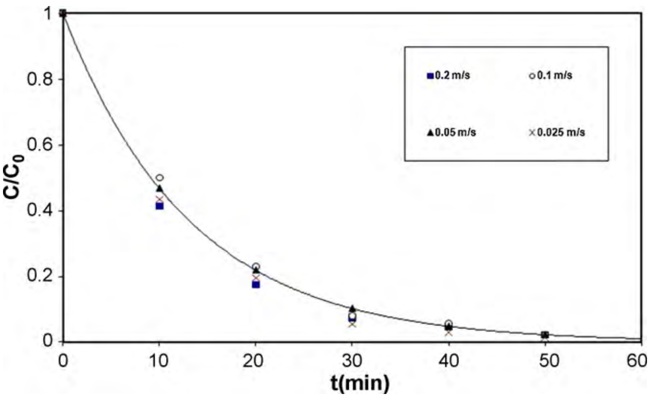

Fig. 7. Ammonia concentration vs. time at different stripping solution velocities (other parameters are at their optimum values).

their optimum conditions). The stripping solution velocity did not noticeably affect ammonia removal. The overall mass transfer coefficient was calculated to be almost 1.47×10^{-5} (m/s) for all of the runs performed.

3.1.6. *Effect of the presence of excess ions*

The scaled ammonia concentration vs. time for different concentrations of an excess electrolyte (sodium chloride) is illustrated in Fig. 8. All other parameters are at their optimum conditions. The presence of salt in the feed solution did not affect ammonia removal. The overall mass transfer coefficient was about 1.47×10^{-5} (m/s) for all the runs performed. Since ammonia in aqueous solution must be converted into NH_3 form in order to permeate through the membrane pores and the presence of excess ions does not influence this phenomenon, the latter variable did not show any adverse effect on the ammonia removal.

It is notable that the presence of excess ions has an adverse effect on most methods used for ammonia removal. As most effluents containing ammonia also include different types of salts, this feature of membrane contactors makes them a superior device for ammonia removal.

3.1.7. *Effect of time*

To investigate the effect of process duration, the removal efficiency of ammonia was calculated at 10, 30 and 50 min. The results were analyzed using ANOVA [16–18]. Comparison of these results gives an understanding of how time influences the process. Fig. 9 illustrates the effect of this variable.

The effect of the pH of the ammonia feed increased as time passed, while the effect of other parameters decreased. These results are explained by the fact that as time increases, the ammonia concentration in the feed solution decreases and the percentage of ammonia converted in to free ammonia, which itself depends on feed pH, becomes the dominant factor in ammonia removal.

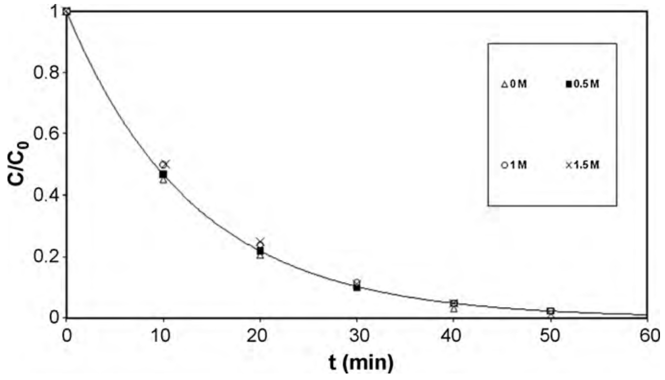

Fig. 8. Ammonia concentration vs. time at different salt concentrations in ammonia feed (other parameters are at their optimum values).

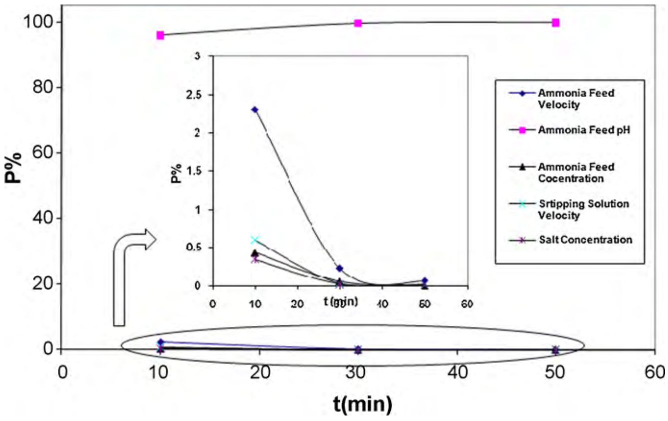

Fig. 9. Changes of each parameter's share on ammonia removal efficiency by time.

3.2. *Second stage of experiments*

The experiments in this stage were performed to further investigate the effect of the pH of the feed solution and velocity of the feed stream on the ammonia removal process. The values of 11, 12 and 13 were set for the ammonia feed pH, while the feed velocities were set at 0.160, 0.116 and 0.213 (m/s). To investigate the effect of ammonia concentration in the stripping solution on the ammonia removal, the values of 3, 5 and 7 vol% were set for sulfuric acid concentration.

3.2.1. *Analysis of the effect of different parameters*

In order to investigate the effect of different parameters on the membrane performance, the amount of overall mass transfer coefficient, *K*, was determined for each run following the procedure described in Section 2.5. Table 3 displays the results obtained. Using the mean response (i.e. arithmetic mean of *K* values for replicated experiments) [16–18] the effect of each parameter upon the overall mass transfer coefficient was characterized. The effect of each parameter on the *K* value can be observed in Fig. 10.

Furthermore, the contribution of each parameter on the overall mass transfer coefficient was determined using ANOVA [16–18] analysis (Table 5). The Qualitek software was used for the purpose.

Fig. 10 shows that the ammonia feed velocity was the most effective parameter; after that ammonia feed pH imposed a slight effect on the overall mass transfer coefficient. These results are not

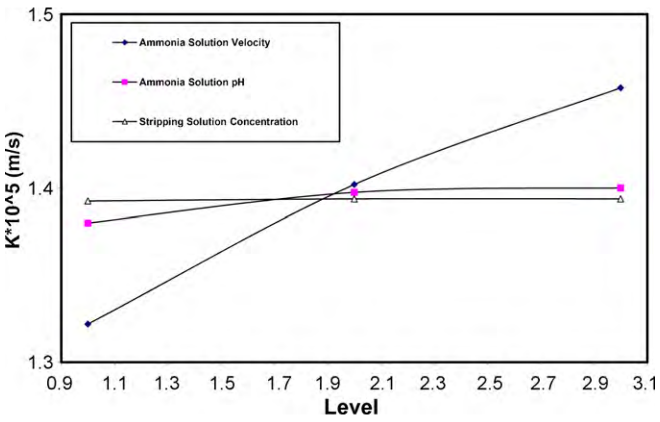

Fig. 10. Effect of different parameters on overall mass transfer coefficient.

Table 5
Each parameter's share on overall mass transfer coefficient.

Parameter	Share (%)
Velocity of the ammonia feed solution	97.7
pH of the ammonia feed solution	2
Concentration of the stripping solution	0.3

correspondent with former results. This has been attributed to the fact that setting the pH to a value higher than 11 does not have a significant influence on the system. It should be notified that the NH_4^+ concentration is considerably low at the pH values higher than 11 and the predominant form is NH_3. According to Eq. (4), higher pHs (higher concentrations of OH^-) shifts the equilibrium to the left side, i.e. higher concentrations of NH_3) [2]. Therefore, the ammonia feed velocity becomes the dominant factor. The stripping solution concentration did not affect the ammonia removal in the range studied. This indicates that as long as there is enough sulfuric acid to react with ammonia, changes in its concentration do not influence the ammonia removal.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-, \qquad (4)$$

$$K = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.82 \times 10^{-5},$$

3.2.2. *Effect of ammonia feed pH and velocity*

The effects of the pH of the feed and feed velocity were investigated at the mentioned conditions for the second stage of experiments while the stripping solution concentration was fixed at 5 vol%. The results are displayed in Figs. 11 and 12. Increasing the pH values over 11 did not noticeably promote the overall mass transfer coefficient. It is due to the way NH_4^+ to NH_3 conversion changes by pH changes. For instance, at pH 11, 98.23% of the ammonia content is in NH_3 form. By increasing the pH value to 12 and 13 the NH_3 form of ammonia becomes 99.82 and 99.98, respectively [2]. At this stage the improving effect of ammonia feed velocity is more obvious.

3.2.3. *Effect of ammonia feed pH*

To study the effect of ammonia feed pH, another set of experiments were performed. The temperature of both solutions was kept at 20 °C and the initial concentrations of the ammonia feed and stripping solutions were set at 800 ppm and 5 vol%, respectively. The stripping solution and ammonia feed velocities were fixed at 0.025 and 0.213 m/s, respectively. The changes of overall mass transfer coefficient with pH value are demonstrated in Fig. 13. This shows that a pH of 11 was the optimum value for the removal.

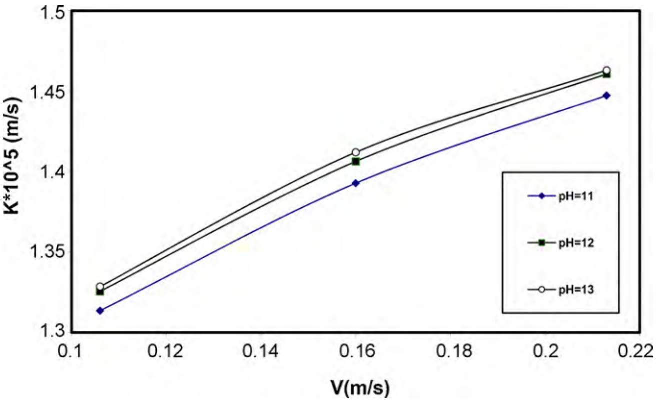

Fig. 11. Effect of ammonia feed pH on overall mass transfer coefficient at different ammonia feed velocities.

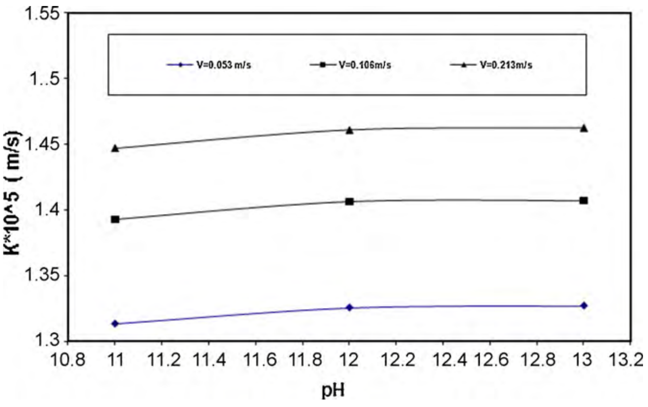

Fig. 12. Effect of ammonia feed velocity on overall mass transfer coefficient at different ammonia feed pH Values.

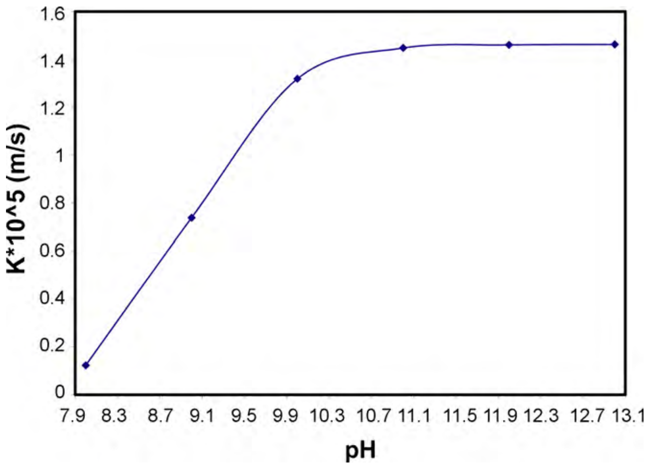

Fig. 13. Effect of ammonia feed pH on overall mass transfer coefficient.

Considering the fact that the beneficial effect of increasing pH value of the solution on the ammonia removal was not so significant for pH value higher than 10, a pH 10 is recommended for ammonia removal process to improve the durability of the membrane life and other instruments.

4. Conclusions

4.1. *The following conclusions can be drawn from the results of the experiments in this study*

1. The elimination of ammonia from wastewater using a microporous hollow-fiber membrane contactor is very efficient. Under optimized conditions the amount of ammonia removal is more than 99%.
2. Increasing the pH value of the ammonia feed solution up to 10, promotes the overall mass transfer coefficient and hence ammonia removal significantly. Setting the pH of the feed solution at values higher than 11 shows only a slight improvement. Further increase in the pH value gives no considerable effect on the ammonia removal. Although the best value of pH is 11, consideration of economical problems associated with higher pH values suggests setting a pH value of 10.
3. Increasing the ammonia feed velocity in the range studied improved the overall mass transfer coefficient and consequently ammonia removal.
4. The stripping solution velocity and concentration had negligible effects on the ammonia removal.

5. The initial concentration of ammonia did not affect the overall mass transfer coefficient. This characteristic of hollow-fiber membrane contactors makes them superior to many other methods which only apply to a restricted range of ammonia concentration.
6. The presence of excess ions had no effect on ammonia removal, while it is a burden for many other techniques of ammonia removal. Since most effluents containing ammonia also include several excessive electrolytes, this property is very advantageous in hollow-fiber membrane contactors.

Acknowledgements

Iranian National Petrochemical Company (NPC) and the Research Council of Iran University of Science and Technology are highly acknowledged for their financial support of this project.

References

[1] P.F. Atkins Jr., A. Scherger Dale, A review of physical–chemical methods for nitrogen removal from wastewaters, Prog. Water Technol. 8 (1997) 713–720.

[2] R. Sedlack, Phosphorus and Nitrogen Removal from Municipal Wastewater: Principles and Practice, 2nd ed., Lewis Publisher, New York, 1991.

[3] Metcalf, Eddy, in: G. Tchobanoglous, F.L. Burton (Eds.), Wastewater Engineering: Treatment, Disposal, Reuse, 3rd ed., McGraw-Hill International Editions, New York, 1991.

[4] D.H. Belhateche, Choose appropriate wastewater treatment technologies, Chem. Eng. Prog. 8 (1995) 32–38.

[5] M.A. Pical, G.M. Faup, Removal of nitrogen from industrial wastewater by biological nitrification–denitrification, J. WPCF 79 (1980) (1980) 213–221.

[6] J.M. Verkerk, Ammonium Removal by Ion Exchange; Reuse of Regenerant, Department of Sanitary Engineering, Delft University of Technology, 2000.

[7] O. Lahav, M. Green, Ammonium removal using ion exchange and biological regeneration, Water Res. 32 (7) (1998) 2019–2027.

[8] S.N. Ashrafizadeh, Z. Khorasani, M. Gorjiara, Ammonia removal from aqueous solution by Iranian natural zeolite, Sep. Sci. Technol. 43 (4) (2008) 960–974.

[9] R.W. Baker, Membrane Technology and Application, 2nd ed., John Wiley, New York, 2004.

[10] S.P. Nunes, K.V. Peinmann, Membrane Technology, Wiley, New York, 2001.

[11] A. Gabelman, S. Hwang, Hollow fiber membrane contactors, J. Membr. Sci. 159 (1999) 61–67.

[12] A. Sengupta, P.A. Peterson, B.D. Miller, J. Schneider, C.W. Fulk Jr., Large-scale application of membrane contactors for gas transfer from or to ultrapure water, Sep. Purif. Technol. 14 (1998) 189–197.

[13] D. Bhattacharyya, D.A. Butterfield, New Insights into Membrane Science and Technology, Elsevier Science, Amsterdam, 2003.

[14] Z. Zhu, Z. Hao, Z. Shen, J. Chen, Modified modeling of the effect of pH and viscosity on the mass transfer in hydrophobic hollow fiber membrane contactors, J. Membr. Sci. 250 (2005) 269–275.

[15] X. Tan, S.P. Tan, W.K. Teo, K. Li, Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water, J. Membr. Sci. 271 (2006) 59–66.

[16] D.C. Montgomery, Design and Analysis of Experiments, 3rd ed., Wiley, New York, 1991.

[17] J.T. Luftig, V.S. Jordan, Design of Experiments in Quality Engineering, McGraw-Hill, New York, 1998.

[18] A.A. Jalali, F. Mohammadi, S.N. Ashrafizadeh, Effects of process conditions on cell voltage, current efficiency and voltage balance of a chlor-alkali membrane cell, Desalination 237 (2009) 126.

[19] S.M. Wang, Y.S. Giang, Y. Ling, Taguchi's method in optimizing the experimental conditions of simultaneous supercritical fluid extraction and chemical derivatization for the gas chromatographic–mass spectrometric determination of amphetamine and methamphetamine in aqueous matrix, Forensic Sci. J. 1 (2002) 47–58.

[20] WPCF, APHA, AWWA Standard Methods for the Examination of Water and Wastewater, 17th ed., Method 4500C, 1989, pp. 4–117.

[21] R. Unal, E.B. Dean, Taguchi approach to design optimization for quality and cost: an overview, in: Annual Conference of the International Society of Parametric Analysts, New Orleans, LA, 1991.